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A Strategy to Protect and Sensitize Near-Infrared Luminescent Nd^{3+} and Yb^{3+} : Organic Tropolonate Ligands for the Sensitization of Ln^{3+} -Doped NaYF_4 Nanocrystals

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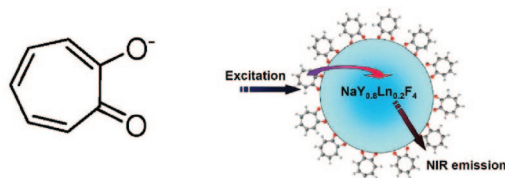
Abstract

A strategy to sensitize and protect near-infrared (NIR) emitting Nd^{3+} and Yb^{3+} is presented. Combining protection provided by the inorganic matrix of NaYF_4 nanocrystals and sensitization from tropolonate ligands capped on their surface, the lanthanide cation centered luminescence was observed through the ligand excitation. The extended lanthanide luminescence lifetimes indicate the success of this strategy.

Lanthanide-based near-infrared (NIR) emitters have a great potential to serve as bioanalytical reporters for several reasons: (i) NIR photons scatter less than visible photons, improving image resolution.¹ (ii) Biological systems have low native autofluorescence in the NIR energy domain,² resulting in higher detection sensitivity due to improved signal-to-noise ratio. (iii) Most luminescent lanthanide complexes are not susceptible to photodecomposition, allowing long or repeated experiments and simplifying sample storage and preparation procedures. Since f–f transitions are Laporte forbidden,³ free Ln^{3+} have low extinction coefficients resulting in low luminescence intensity. Therefore, it is necessary to sensitize these cations through a suitable chromophore (“antenna effect”),⁴ an area of research that has been highly active in recent years.⁵ However, this approach has intrinsic limitations because lanthanide luminescence is easily quenched through nonradiative routes when the cations are in close proximity to the vibrational overtones of -OH, -NH, and -CH groups present in the sensitizing ligand and/or solvent.⁶ This effect is particularly dramatic for NIR emitting Ln^{3+} because of relatively small energy gaps between ground and excited electronic states.⁶ To alleviate this limitation, Ln^{3+} have been incorporated into inorganic matrices, such as LnF_3 ,⁷ Ln_2O_3 ,⁸ LnPO_4 ,⁹ LnVO_4 ,¹⁰ TiO_2 ,¹¹ and Zeolites.¹² These materials protect lanthanide cations from sources of nonradiative deactivation; however, they have either limited (e.g., LnVO_4) or no absorbance in the UV range. Thus, these inorganic materials are not able to sensitize lanthanide luminescence with the efficiency of organic sensitizers.

Here we introduce a strategy to overcome the limited lanthanide sensitization by binding organic tropolonate chromophoric groups to the surface of NaYF_4 nanocrystals (NCs), doped with NIR emitting Nd^{3+} or Yb^{3+} (Scheme 1). Tropolonate (Trop[−]) was chosen as a capping ligand since it has been previously demonstrated to be a suitable sensitizer for several lanthanide cations emitting in the NIR range when coordinated in $\text{KLn}(\text{Trop})_4$ complexes.¹³ These novel systems use the NaYF_4 matrix to protect Ln^{3+} from nonradiative deactivations, while a chromophoric coating sensitizes their luminescence.

A synthetic method to prepare Nd^{3+} or Yb^{3+} doped NaYF_4 NCs was developed on the basis of a recently reported synthesis of NaYF_4 NCs (see Supporting Information).¹⁴ The Trop[−] capped NCs were synthesized using the following procedure. Tropolone was dissolved in methanol, then deprotonated with an equimolar amount of KOH in methanol. Chloroform was added to obtain a 1/1 (v/v) MeOH/ CHCl_3 solvent mixture. This solution was added to a purified solution of NCs dispersed in chloroform. The resulting mixture was sonicated for 2 h, and the solvent was



Scheme 1. Molecular Structure of Tropolonate and Schematic Illustration of Tropolonate Capped Nd^{3+} - or Yb^{3+} -Doped NaYF_4 Nanocrystals and the Energy Transfer Process

removed under vacuum. The resulting solid was washed with ethanol and DMSO and dried under vacuum for 24 h. The binding of the Trop[−] groups to the surface of nanocrystals was monitored through FT-IR spectroscopy (Figure S1, Supporting Information). Upon reaction, the absorption bands assigned to the original capping ligands of the NCs (oleic acid, oleylamine, and octadecene) present at 2924 and 2854 cm^{-1} disappear and are replaced by the characteristic absorption bands of Trop[−] at 1595 and 1510 cm^{-1} .

The XRD patterns (Figure 1, right) of the uncapped and capped $\text{NaY}_{0.8}\text{Ln}_{0.2}\text{F}_4$ NCs (Ln: Nd or Yb) reveal the formation of cubic $\alpha\text{-NaYF}_4$ (space group: $Fm\bar{3}m$). All diffraction peak positions and intensities agree well with calculated values.¹⁵ Transmission electron microscopy (TEM) images (Figure 1, left) of both uncapped and capped NC samples also indicate that the obtained nanocrystals are of single-crystalline nature with high crystalline size uniformity. They are relatively monodisperse with roughly spherical shape. The average sizes are 6.1 ± 0.6 nm, 6.0 ± 0.6 nm, 5.3 ± 0.7 nm, and 5.3 ± 0.6 nm for $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, Trop[−] capped $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NCs, and Trop[−] $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, respectively (Figure S3, Supporting Information). Such relatively small sizes are compatible for use in many bioanalytical applications.

The UV–vis absorption spectra (Figure 2) of Trop[−] capped NCs in DMSO reveal the presence of two bands with apparent maxima centered around 323 and 384 nm, similar to those observed for $[\text{Ln}(\text{Trop})_4]^-$ confirming the presence of Trop[−] on the surface of NCs. Upon excitation at 340 nm, the characteristic sharp NIR emission bands arising from Nd^{3+} or Yb^{3+} were observed (Figure 2). The excitation profiles of lanthanide luminescence in both Nd^{3+} and Yb^{3+} doped NCs are similar (Figure S3), demonstrating that the lanthanide cations are sensitized through the same source: the electronic structure of the Trop[−] ligand. For Yb^{3+} , there is a significant energy gap between the energy donating levels of Trop[−] and its accepting levels. Energy transfer over this large gap could be explained by phonon-assisted or electron-transfer mechanisms.¹⁶

The lifetimes of the luminescence arising from Nd^{3+} and Yb^{3+} in Trop[−] capped NCs and in $[\text{Ln}(\text{Trop})_4]^-$ complexes were determined in DMSO and are reported in Table 1. It is important to note that the Nd^{3+} and Yb^{3+} luminescence decays in $[\text{Ln}(\text{Trop})_4]^-$ complexes are best fit as monoexponential decays, indicating a unique coordination environment around the central Ln^{3+} .¹³ Since there should be more than one coordination environment for Ln^{3+}

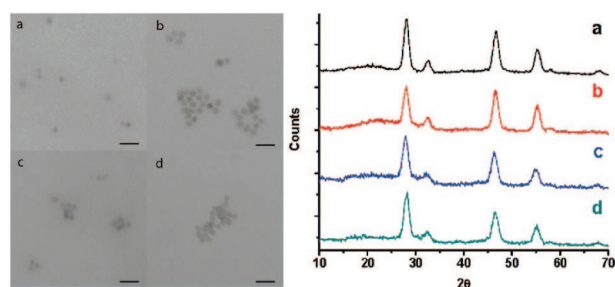


Figure 1. Transmission electron microscopy images (left, scale bar: 20 nm) and the X-ray diffraction patterns (right) of uncapped and capped NCs. (a) $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, (b) Trop[−] capped $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, (c) $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NCs, (d) Trop[−] capped $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NCs.

Table 1. Luminescence Lifetimes (μs) of the Complexes and Trop[−]-Capped NCs and Contribution to Luminescence Intensity in Brackets. $\lambda_{\text{ex}} = 354 \text{ nm}$

	$\text{NaY}_{0.8}\text{Ln}_{0.2}\text{F}_4$ NC	$\text{KLn}(\text{Trop})_4$
Yb^{3+}	68(3), [80(2)%] 4.1(4), [20(2)%]	12.43(9)
Nd^{3+}	12.6(9), [22(1)%] 3.7(2), [63(6)%] 1.1(2), [15(6)%]	1.10(4)

in the NCs (i.e., core and surface), multiexponential decay profiles are expected. The experimental results reflect this hypothesis. For Yb^{3+} in the NCs, the experimental decay was best fitted as biexponential function. The longest component is attributed to the luminescence decay from cations in the NC core and is the major contribution to the overall intensity. The second component is significantly shorter and can be attributed to Yb^{3+} with a lower level of protection from nonradiative deactivation, likely located at the surface of the nanocrystals. The experimental decay recorded for Nd^{3+} in the NCs is best fit with a triple exponential decay. Similar to Yb^{3+} , there is a long component which corresponds to luminescence decay from Nd^{3+} in the nanocrystal matrix. The two shorter components are assigned to Nd^{3+} at or near the NCs surface in different coordination environments. Since Nd^{3+} , unlike Yb^{3+} , has a large number of excited states, and thus additional routes for non-radiative deactivations, it may be more sensitive to coordinating ligands than Yb^{3+} resulting in additional lifetime components.

Globally, significantly longer luminescence lifetimes were observed for the Trop[−] capped $\text{Yb}^{3+}/\text{Nd}^{3+}$ doped NCs than for the corresponding molecular complex $[\text{Ln}(\text{Trop})_4]$. The longest components among the luminescence lifetimes were more than 5 times longer for Yb^{3+} and more than 11 times longer for Nd^{3+} . These values prove that our strategy to increase protection around the lanthanide cations through their incorporation in NCs is successful.

In conclusion, we have demonstrated the success of an innovative strategy to protect and sensitize NIR emitting Nd^{3+} and Yb^{3+} cations via doping in NaYF_4 NCs coated with sensitizing tropolonate chromophores. The NC matrix protects the Ln^{3+} from nonradiative deactivation via high-energy vibrations of solvent molecules and/or of organic ligands, as proven by the longer luminescence lifetimes. Through this work, we have established proof that it is possible to combine the antenna effect provided by organic chromophores with the protection from an inorganic matrix, thereby reducing the usual limitations of NIR lanthanide luminescence in coordination complexes. This is a general strategy that can be expanded for application to different combinations of organic chromophores, lanthanide cations, and inorganic matrices. The NCs have a relatively small size, and combined with the proper choice of ligand system(s) to give the capped NCs water solubility, it will be possible to extend this methodology for bioanalytical applications.

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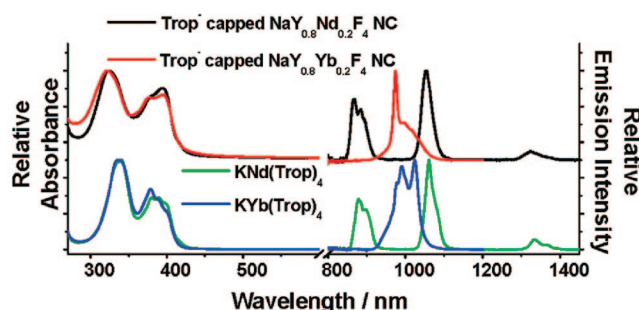


Figure 2. Normalized UV-vis absorption (left) and NIR luminescence emission spectra (right) of the complex (bottom) ($\lambda_{\text{ex}} = 340 \text{ nm}$, 10^{-4} M) and Trop[−]-capped NCs (ca. 1 g L^{-1}) in DMSO (top).

images. We also thank Prof. Richard A. Butera (Dept. of Chemistry, University of Pittsburgh) for his insight in the interpretation of XRD data. Funding was provided through the University of Pittsburgh and through the NSF (award DBI 0352346). Jian Zhang was supported through an Andrew Mellon Predoctoral Fellowship.

Supporting Information — Including chemicals used, instruments, methods, experimental spectroscopic procedures, and synthesis presented following the References.

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Supporting Information for

A Strategy to Protect and Sensitize Near Infrared Luminescent Nd³⁺ and Yb³⁺ : Organic Tropolonate Ligands for the Sensitization of Ln³⁺ Doped NaYF₄ Nanocrystals

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Experimental

Chemicals

Tropolone, KOH standard solution in methanol (0.100 N), Y₂O₃, Nd₂O₃, Yb₂O₃, oleic acid (90%), oleylamine (>80%), 1-octadecene (>90%), trifluoroacetic acid (99%), NaCF₃COO (>97%) were purchased from Aldrich. The synthesis was carried out using standard oxygen-free procedures. All the solvents, absolute ethanol and chloroform, were used as received. Y(CF₃COO)₃, Nd(CF₃COO)₃ and Yb(CF₃COO)₃ were prepared according to literature method¹.

Synthesis of Nd³⁺ or Yb³⁺ doped NaYF₄ nanocrystals^{2,3}

Sodium trifluoroacetate (0.136g, 1.0mmol), Y(CF₃COO)₃ (0.386g, 0.8 mmol) and Nd(CF₃COO)₃ (0.107g, 0.2 mmol) or Yb(CF₃COO)₃ (0.113g, 0.2 mmol) were then added to the reaction vessel with octadecene (5.05 g, 20 mmol), oleic acid (2.82g, 10 mmol) and oleylamine (2.68 g, 10 mmol). The mixture was heated to 100 °C under vacuum and stirred for 30 min to remove the residual water and oxygen. The solution was then heated to 325 °C under argon and maintained at this temperature for 40 min. Subsequently, the mixture was allowed to cool to room temperature, and the resulting NCs were precipitated by addition of ethanol and isolated via centrifugation. The resulting solid was then washed twice with ethanol and dried under vacuum for 24 h.

Methods

UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument.

Lanthanide luminescence emission and excitation spectra were measured using a Jobin Yvon-Horiba Fluorolog-322 spectrofluorometer (detector for NIR domain: DSS-IGA020L, Electro-Optical Systems, Inc.).

The luminescence lifetime measurements were performed by excitation of solutions in 1 cm quartz cells using a Nd:YAG Continuum Powerlite 8010 Laser (354 nm, 3rd harmonic) as the excitation source. Emission was collected at a right angle to the excitation beam and emission wavelengths were selected using a Spectral

Products CM 110 1/8 meter monochromator. The signal was monitored by a cooled photomultiplier (Hamamatsu R316-2) coupled to a 500 MHz bandpass digital oscilloscope (Tektronix TDS 754D). The signals (15,000 points each trace) from at least 500 flashes were collected and averaged. Luminescence decay curves were imported into Origin 7.0 scientific data analysis software. The decay curves were analyzed using the Advanced Fitting Tool module and fitted with mono-, bi- and tri-exponential modes. Of the three modes, the lifetime value was chosen based on the best fit of the decay curve on the criteria of the minimum χ^2 statistical parameter. Lifetimes are averages of at least three independent determinations.

Powder X-ray diffraction (XRD) patterns of the dried powders were recorded on a Philips X'pert diffractometer (PW3710) with a slit of $1/2^\circ$ at a scanning rate of 3° min^{-1} , using Cu K α radiation, $\lambda=1.5406 \text{ \AA}$). Samples were evaporated or pressed onto glass microscope slides.

TEM method: A small drop of solution containing the sample was placed on a carbon coated copper grid. After several seconds, the drop was removed by blotting with filter paper. The sample that remained on the grid was allowed to dry before inserting the grid into the microscope. The grids were viewed on a transmission electron microscope (Hitachi H-7100 TEM, Hitachi High Technologies America, 5100 Franklin Drive, Pleasanton, CA, 94588) operating at 75 kV. Digital images were obtained using an AMT Advantage 10 CCD Camera System (Advanced Microscopy Techniques Corporation, 3 Electronics Ave., Danvers, MA, 01923) and NIH Image software. Particle diameter was measured using a negatively stained catalase crystal as a calibration standard.

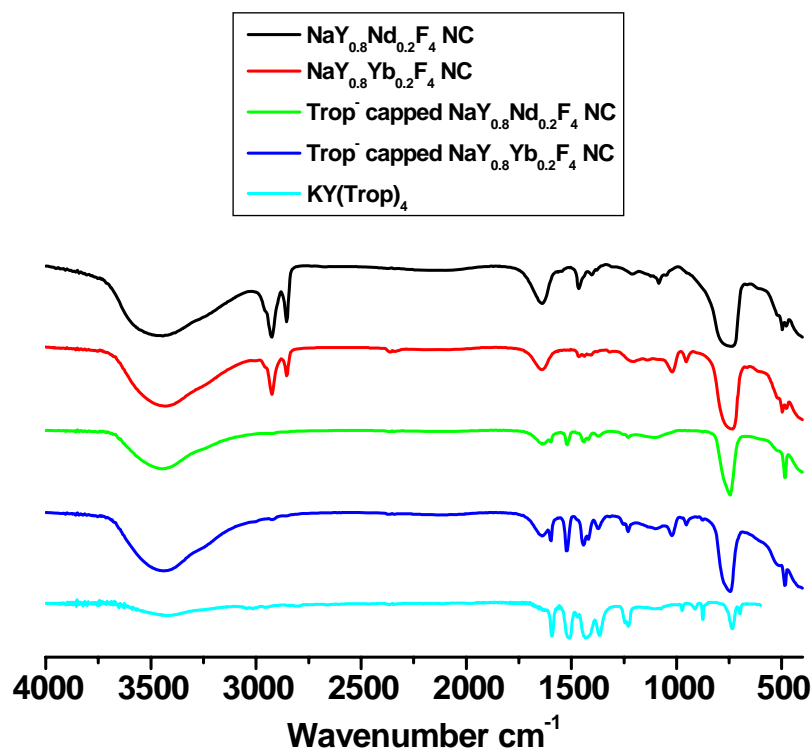


Figure S1. FT-IR spectra of $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4 \text{ NCs}$, $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4 \text{ NCs}$, Trop⁻ capped $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4 \text{ NCs}$, and Trop⁻ capped $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4 \text{ NCs}$. For comparison, the FT-IR spectra of $\text{KY}(\text{Trop})_4$ is also depicted.

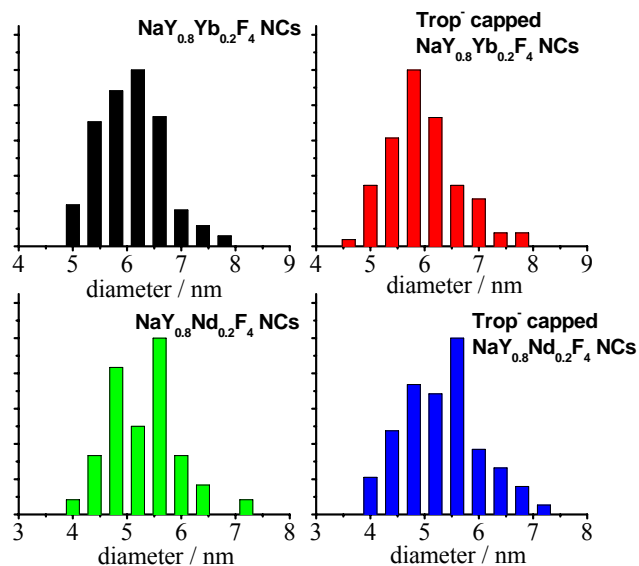


Figure S2. Histogram of the nanocrystal size distribution derived from the TEM images.

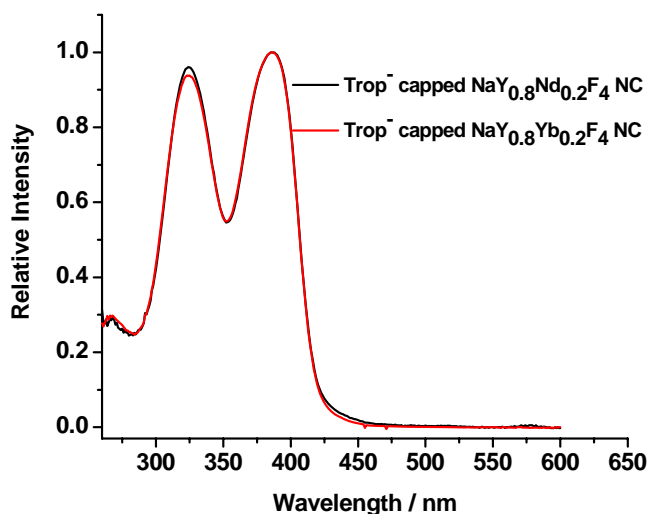


Figure S3. Normalized NIR luminescence excitation spectra of the complex Trop⁻ capped NCs (c.a. 1 gL⁻¹) in DMSO. (Emission wavelength were set as 1055 nm and 975 nm for Trop⁻ capped $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NC and Trop⁻ capped $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NC respectively).

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